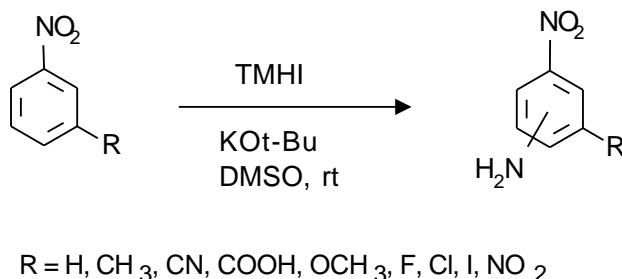


New Insensitive Energetic Materials via Vicarious Nucleophilic Amination of Nitroaromatics*

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Vicarious Nucleophilic Substitution (VNS) of hydrogen is an established method for introducing carbon and nitrogen moieties into electrophilic aromatic rings at unfunctionalized ring positions. We have examined the amination of several nitroaromatic and nitroheteroaromatic systems using this method. During the course of this work, we developed a novel reagent--1,1,1-trimethylhydrazinium iodide (TMHI)--which has proven to be a highly reactive and readily accessible reagent for VNS amination. The general utility of TMHI was examined by reacting it with a series of *meta*-substituted nitrobenzenes (Scheme I).



Scheme I

The use of TMHI was also applied to the synthesis of energetic materials. In our first example, picramide is converted to 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) in several hours at room temperature. This represents a new and potentially inexpensive route to TATB, which is considered to be the standard in insensitive high explosives.

To further test its utility, TMHI was reacted with other nitroarenes, including 2,4,6-trinitrotoluene (TNT) and 3,5-dinitropyrazole. By analogy with TATB, it is predicted that the amination products of these compounds will be less impact-sensitive than their precursors yet have comparable performance.

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